APR 5 1926

61—3

Proceedings of the American Academy of Arts and Sciences.

Vol. 61. No. 3.—February, 1926.

THE EFFECT OF PRESSURE ON THE VISCOSITY OF FORTY-THREE PURE LIQUIDS.

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The cost of publication of this research has been met in part with the help of a grant from the National Academy of Science.

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VOLUME 61.

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Presented October 14, 1925. Received November 16, 1925.

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Introduction.

Among the non-thermodynamic properties of a liquid, the viscosity is one of those which might be expected to be of most significance, and is one which has been most studied experimentally. There are various lines of evidence which suggest that the viscosity of a liquid is more intimately connected with the specific properties of the molecules than is the viscosity of a gas. It is known that the mechanism of viscous resistance in a liquid must be different from that in a gas, but there are no theories at present capable of giving an adequate account of the phenomena. It is to be expected that the information given by the change of viscosity produced by pressure will be especially significant, since under pressure the molecules are brought into closer contact, and any peculiarities in their specific relations accentuated. There have been, however, only a few measurements of the effect of pressure on the viscosity of pure liquids, and these over only a comparatively small range of pressure.[1] The effect of pressure on the viscosity of a number of lubricating oils has been recently determined over a range sufficient to change the viscosity many fold,[2] but oils are not simple substances, and the results obtained with them cannot be easily interpreted, although information of this character is evidently of much importance technically.

In this paper the effect of pressure has been studied on some forty-three pure liquids, most of them organic, but including water. In

addition, petroleum-ether and kerosene have been studied because of their interest in connection with high pressure apparatus. The method used has demanded that all the liquids be electrical non-conductors. The range of the measurements is 12000 kg./cm.^{2} (unless the liquid freezes at a lower pressure, as is often the case), and measurements have been made at 30° and 75°, thus giving both the effects of pressure and temperature. It may be said in general that the effects of pressure on viscosity are greater than on any other physical property hitherto measured, and vary very widely with the nature of the liquid. The increase of viscosity produced by 12000 kg. varies from two or three fold to millions of fold for the liquids investigated here, whereas such properties as the volume decrease under 12000 seldom vary by as much as a factor of two from substance to substance.

The Method and the Apparatus.

None of the methods previously used for the measurement of the effect of pressure on viscosity was adapted to the greater pressure range of this work, in general the apparatus being too bulky or too cumbersome in operation, requiring for example that the pressure chamber be reopened and the apparatus refilled for every new determination at a new pressure. The apparatus adopted does not give the absolute viscosity, but does give the relative viscosity, which is all we are interested in here, and is shown in Figure 1. The general idea of the method is very simple; in a steel cylinder of approximately 6 mm. internal diameter, filled with the liquid under investigation, there is a steel cylindrical weight separated from the walls of the cylinder by a narrow annular space. The time of vertical fall of the weight from one end of the cylinder to the other is determined; the time is a measure of the viscosity.

The pressure producing apparatus is so mounted and connected with the viscosity cylinder that it may be rotated through 180°, so that after the time of fall of the weight has been determined the apparatus may be reversed, and the time of fall in the opposite direction determined. This may be repeated as often as desired, allowing an indefinite number of readings at any pressure with the same set-up.

The time of fall is determined electrically. At each end of the cylinder there is an electrically insulated terminal D against which the weight rests at the end of its fall. In this position electrical connection is made from the walls of the cylinder through the weight to the terminal, and the completion of this connection may be made to

operate a suitable timing device. It is necessary, therefore, that the weight be in close enough contact with the cylinder to permit

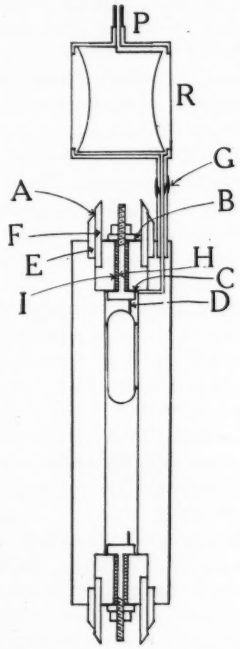

FIGURE 1. Section of viscosity apparatus.

passage of current, but at the same time be capable of free fall. With the electrical arrangements used it was necessary that the contact

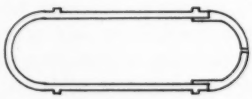

FIGURE 2. Detail of falling weight of viscosity apparatus.

between weight and cylinder be closer than 0.0025 cm. The weight, Figure 2, was provided with three small projecting lugs* at the top

* Shown as two in the figure for convenience of drawing.

and bottom ends, which act as guides to keep the weight concentric as it falls, and through which electrical contact is made with the cylinder. By putting the stop *D* against which the weight rests at the end of its fall off center, it was ensured that the lugs on one side of the weight were pressed more firmly against the cylinder, thus making better contact. In order to keep the time of fall within reasonable limits, different weights were used according to the absolute viscosity of the liquid, the annular space between weight and cylinder varying between 0.0125 cm. for water to 0.075 cm. for the more viscous liquids such as glycerine. There was further provision for variability in the viscosity of the liquid by making the weight hollow (see detail in Figure 2), and changing its total weight by placing within the cavity appropriate weights of tungsten or gold. The hollow weight was made in two pieces, of the same material as the cylinder. The main body of the weight, with the lugs, was milled from one piece, and a cap to close the cavity was made a tight push fit for the body of the weight. The external shape of the cap was made as much like that of the other end as possible, but the two ends were never exactly alike, because for one thing it was necessary to provide a small hole in one end by which the interior might be filled. The times of fall in the two directions were, therefore, never exactly the same; the difference was not often more than one per cent.

The insulating plugs at the two ends of the cylinder are shown in the figure. It is the function of these plugs not only to provide a terminal electrically insulated from the cylinder, but to prevent the liquid under investigation in the cylinder from mixing with the pump liquid in which the cylinder is immersed. The central stem of the the plug, *H*, is of brass, with the projecting terminal of platinum, *D*, insulated by a sleeve of pipestone, *I*, and flat washers of mica *B* and *C*. The mechanical separation of the liquid inside from that outside is provided entirely by the washer *C*. The seats on which the mica washers rest are ground flat; the washers are made as tight as possible initially with the nut on the stem, and become still tighter under pressure because of the differential compressibility of the brass stem and the steel of which the surrounding parts of the apparatus are made. The insulating plug was soldered into the end of the cylinder; in this way the liquid under investigation came in contact only with metals or mica, and was kept pure. The soldering and unsoldering were facilitated by two german silver sleeves *E* and *F* permanently soldered to the cylinder and the plug respectively. The soldered connection between cylinder and plug was made and broken

at *A*. This could be easily done since in the first place german silver is easy to solder, and in the second place is a poor conductor of heat, so that the soldering could be done rapidly with a soldering copper without seriously heating the rest of the apparatus. The unsoldering was facilitated by a special soldering copper, of cylindrical shape to fit the sleeve.

The liquid under investigation, which fills the inside of the cylinder, must be kept from contact with the surrounding liquid by which pressure is transmitted, but at the same time must freely receive the pressure. This was done by means of a reservoir, *R*, of very thin pure tin, attached to the upper end of the cylinder as shown. The pressure is transmitted from the liquid on the outside to that on the inside through the tin walls of the reservoir, which offer so little resistance that the pressures outside and inside are the same within less than 1 kg./cm.^{2} This device of the reservoir has already been used in connection with measurements of the effect of pressure on the thermal conductivity of liquids, and will be found described in greater detail in that paper.[3] The connection from the reservoir to the cylinder was through a tube of german silver; this connection, *G*, was resoldered and a new reservoir made at each new filling of the apparatus with a new liquid. The apparatus was filled through the fine tube, *P*, of german silver at the top of the reservoir. The filling liquid was placed in a glass thistle connected in such a way with rubber tubing to the pipe at the top of the reservoir that practically no liquid came in contact with the rubber, and then the whole combination was placed bodily under the receiver of an air pump. It was filled by exhausting the receiver, the air inside the cylinder bubbling out through the liquid in the thistle, and then readmitting air to the receiver, driving the liquid into the reservoir and the cylinder. The receiver was exhausted to such a point that the liquid boiled vigorously, and this was repeated a number of times, so that the liquid was nearly air free. The reservoir was then closed by soldering into the top of the pipe, *P*, a brass plug, the outside of the pipe being kept cool in a simple way with water, so that the liquid inside could not boil during the soldering. The cylinder and the reservoir, filled with the liquid, were now attached with screws to an insulating plug, not shown, but essentially like the one described in the paper on thermal conductivity. Soldered connection was made from the insulated terminals of the cylinder to the insulated terminals of the plug, and the plug, with cylinder and reservoir as one self-contained unit, were screwed into the large pressure cylinder.

The large pressure cylinder was connected with a pipe to the pressure generating apparatus and the pressure gauge, which were the same as that used in previous work. They were now mounted horizontally, instead of vertically, and were so arranged that they could be rotated about the connecting pipe as an axis. During this rotation the hydraulic press with which pressure was produced had to be disconnected from the hand pumps which were the source of pressure. This was made possible by valves mounted to rotate with the press, so that the pressure produced by the pump could be maintained after the transmitting pipe has been disconnected. The large pressure cylinder which contained the viscosity apparatus was T-shaped; there was a side connection at which entered the pipe connecting to the pressure producing apparatus, which acted as the long arm of the *T*, which was horizontal and about which rotation took place. The main body of the cylinder acted as the cross arm of the T, and by rotation was changed from one vertical position to the inverse. The falling weight within the viscosity apparatus fell along the axis of the cross arm of the T. The viscosity cylinder was kept at constant temperature by the conventional stirred bath and regulators; the horizontal connecting pipe entered the bath through a simple stuffing box.

The timing apparatus was a comparatively simple affair. A Warren clock, which is essentially a small motor running synchronously with the commercial 60 cycle alternating current source, was connected to the second hand shaft of an ordinary clock movement. The Warren clock made one revolution per second, so that the clock movement rotated at 60 times the normal speed. The circuit of the Warren clock was made and broken through a relay operated by the circuit in which was the falling weight of the viscosity apparatus. Since the Warren clock did not stop immediately when the circuit was broken, it was necessary to provide a mechanical stop; this was done by an arm with a pointed end pulled by a spring into the teeth of one of the gears of the clock movement. This was operated by a relay in series with the other relay. To provide against too great mechanical shock to the clock movement on stopping, there was a spring in the connection between the Warren clock and the clock movement. Since there were 60 teeth in the gear used for stopping purposes, the smallest time interval capable of being distinguished was 1/60 second, so that the necessary error in the determination of a single time interval was not over 1/120 second.

Considerable difficulty was found in getting a proper source of current to operate the relay through the contact made by the falling

weight. If the weight is to fall freely, there is considerable necessary contact resistance between the lugs and the walls of the cylinder. Direct current is not suitable, for if the voltage is high enough to jump the gap an arc follows, which may decompose the liquid or make the weight stick to the walls of the cylinder. After some trial, the alternating current delivered by a small bell ringing magneto of the type used in insulation testing was found suitable. The magneto was driven by a variable speed motor, connected through a belt and cone pulleys in such a way as to give a wide variation of speed. The speed was chosen as low as possible to give positive contacts, thus avoiding as much as possible contamination of the liquid by sparking. The use of such a source made it necessary to use in operating the Warren clock a relay sensitive to alternating current; an old telephone relay was found suitable.

There were various possible sources of error in the starting and stopping of the clock and the operation of the various relays, so that a calibration of the timing device was necessary. This was done by means of a second Warren clock, also rotating at one revolution per second. To the axle of this was attached a copper disc, one quarter of the periphery of which was insulated from the rest. Contacts made from the axle to the periphery gave a current which during every second was interrupted for exactly one-quarter second. The calibrating device could be connected to the timing device instead of the weight of the viscosity apparatus, and thus the clock tested by measuring known intervals of ¼ second. The calibration was made by the measurement of 50 such intervals. The error in the timing apparatus depends on the speed of the magneto; in by far the majority of cases the error in the average of 50 readings was only a few thousandths of a second, and in the worst case it never exceeded 0.050 second. Of course the error in a single interval could be considerably more. Since the error in the timing device is an absolute and not a relative matter, it is much more serious at the short intervals. The procedure was adopted of calibrating the clock with 50 ¼ second intervals after every readjustment of pressure when the absolute time of fall was less than 5 seconds, and at less frequent intervals for longer falls. If the time of fall was less than 5 seconds, 50 fall times of the weight were measured. The error in the finally corrected time of fall could not have been more than 0.002 or 0.003 seconds.

In addition to the corrections of the timing device there were a number of other corrections. What is desired is to so correct the measured time of fall that the finally corrected value shall be propor-

tional to the viscosity of the liquid at different pressures and temperatures. This demands, among other things, that the weight be falling for the entire time under a constant force with a constant velocity. Under the actual conditions the weight did not fall for the entire distance under a constant force, because while the cylinder was being rotated to start a new fall the weight started to fall before a completely vertical postition was reached, and therefore was falling under a diminished effective gravity until the completely vertical position was reached. The correction for this effect could be determined by measuring the time interval between the weight starting to fall and the cylinder reaching a completely vertical position. This was done electrically in a simple way by measuring, with the same timing apparatus as was used to time the falling weight, the interval between breaking of contact by the weight as it began to fall, and the reaching of a vertical position, which could be determined by making the rotating part come against a stop at the end of its rotation. Since the rate of rotation during the last part of the 180° inversion was approximately constant, the time of fall was corrected by subtracting from the measured time interval one-half the interval between starting to fall and reaching the completely vertical position. This correction so determined was 0.05 second.

Another correction is that due to the inertia effect at the beginning of fall. Because of the inertia of the weight a certain amount of time is needed to build up the final velocity. The correction may be determined theoretically from the equation of motion of the falling weight in a vscous liquid, and with the dimensions used was very small. The distance of free fall was 3 cm. In only one or two cases in these experiments was a time of fall used of less than one second. The correction for the acceleration effect is — 0.003 second for a fall time of 1 second, — 0.0015 at 2 seconds, and inappreciable above this.

The corrections so far discussed are important only at short times of fall. The largest correction is for the change of buoyancy of the liquid on the falling weight as the density of the liquid changes under pressure or with temperature. This correction is a percentage correction and is naturally greatest at the highest pressures. It may be shown that the exact expression for the correction, which is somewhat more complicated, reduces to the simpler form:

$$\frac{\rho_p - \rho_0}{\rho_0}\left[\frac{\dfrac{W_1}{D_1}+\dfrac{W_2}{D_2}}{\dfrac{W_1+W_2}{\rho_0}-\left(\dfrac{W_1}{D_1}+\dfrac{W_2}{D_2}\right)}\right],$$

with an error of less than 1% of the correction. This is accurate enough, since the total correction does not rise to over 5%. In this formula W_1 is the weight of the hollow steel shell, and D_1 the density of the steel, W_2 the weight and D_2 the density of the core of the shell (either of tungsten or gold), ρ_0 is the atmospheric density of the liquid and ρ_p its density under pressure. The compressibility of the metal of the falling weight does not enter within the limits of error.

In the following, the relative viscosities for any liquid are expressed in terms of the viscosity at 30° at atmospheric pressure as unity. The results of the run at 75° were corrected by a double application of the above formula; a first application corrected the viscosity at atmospheric pressure at 75° for the change in buoyancy of the liquid due to thermal expansion at atmospheric pressure (this correction was very small), and a second application then corrected the readings obtained under pressure for the change of density of the liquid produced by pressure at 75°. Within the limits of error, the percentage correction for the pressure effect is the same at 30° and 75°.

The compressibility of about a dozen of the liquids of this investigation have already been measured,[4] so that for these liquids the pressure correction could be exactly computed. The compressibility of the other liquids has not been measured to high pressures, so that for them some sort of estimate had to be made of the correction. This estimate could be made with considerable confidence because it is known that $(\rho_p - \rho_0)/\rho_0$ as a function of pressure does not vary greatly from liquid to liquid among such organic liquids as those used here. The procedure in calculating the correction for a liquid whose compressibility had not been measured was to substitute into the formula above the value of ρ_0 of the liquid (obtained from the tables) and to use for $(\rho_p - \rho_0)/\rho_0$ the corresponding value for that one of the twelve liquids whose compressibility had been measured which was most nearly like the liquid in question. In selecting the most similar liquid, weight was given both to the chemical constitution and to the compressibility at low pressures in those cases in which this had been determined by other observers. It was not difficult to select a similar liquid in practically every case except that of glycerine. The low pressure compressibility of glycerine is so much less than that of any other of the liquids that an estimate of the correction did not seem safe, and the compressibility was therefore determined by special experiment, and will be described in detail later.

The correction for buoyancy rises to as much as 5% in only a few

extreme cases. It was found by trial that the correction could be determined with an error of less than 0.1% in the final result over the entire range by actually computing it at only 2000, 6000, and 12000 kg., and then passing a smooth curve through the four points (the correction is zero at atmospheric pressure). It must be recognized that in some cases the error in the estimated correction may, because of an incorrect assumption about the compressibility, be over 0.1%, although I do not believe that this is often the case. For this reason, the corrections assumed for buoyancy are listed with the final data for each liquid together with the falling weights, so that at some future time, when the compressibility has been exactly determined, a more exact correction may be applied if necessary.

In computing the temperature correction for buoyancy at atmospheric pressure the effect of the thermal expansion of the steel is negligible, and only the thermal expansion of the liquid affects the result. The correction tends to become large when the density of the liquid is high, and small when the falling weight is of high density, as when a gold or tungsten core were used. The volume expansion of most of the liquids of this paper, with the exception of water, is about 5% between 30° and 75°, and this value was assumed for all except water. The correction was calculated by combining this value for the expansion with the particular weight and initial density of each liquid. The correction is 0.5% for nearly all the liquids, but for a substance with so extreme a density as ethylene dibromide rose to a maximum of 1.8%.

Finally a correction has to be applied for the change of dimensions of the apparatus under pressure. Since the cylinder and the weight were made of the same material (it is only the change of the *external* shape of the falling weight which is effective and so the core need not be considered), and since the pressure is hydrostatic, only the absolute dimensions of the apparatus change under pressure but the geometrical proportions remain unaltered. The way in which the time of fall varies with the absolute dimensions may be found by a dimensional argument. The time of fall, t, is a function of the viscosity of the liquid, η, the absolute linear dimensions, l, various dimensionless shape factors, and the total force, f, with which gravity pulls on the falling weight. Writing out the dimensions of η and f in terms of mass, length, and time, we see that

$$t \propto \eta f l^2.$$

The time of fall is therefore proportional to the square of the linear

dimensions. Under pressure the linear dimensions become smaller, and so the time of fall becomes smaller. Hence the observed time of fall under pressure is to be corrected by adding a percentage amount equal to twice the linear compression of the steel of the cylinder at the pressure in question. This correction is linear with pressure, independent of the temperature, and at 12000 kg. is 0.46%.

In addition to the corrections described above peculiar to these measurements of viscosity, there are other corrections common to all high pressure measurements, which have been described in sufficient detail previously.[5] All the corrections together do not amount to over 10% in the extreme case, and more often were of the order of 3 or 4%.

Experimental Procedure.

The first operation of a pressure run was filling the viscosity cylinder with the liquid. This had to be done with extreme care to avoid the introduction of bits of mechanical dirt which might hinder the free fall of the weight. In the preliminary work a good many unsuccessful attempts were made before the appropriate procedure was found. The apparatus was first disassembled from the preceding run by unsoldering the insulating plugs and the tin reservoir. The inside of the cylinder, which is brightly polished, was scoured with a linen rag and whiting powder, and then all loose particles wiped out with a clean linen rag and a camel's hair brush. The brass terminals and the flat faces of the insulating plug were polished bright with the finest French emery paper. The reservoir was remade by unsoldering the thin tin wall, partially deformed from the previous run, and brightly scouring with French emery paper the top and bottom plates and the central core. The reservoir was now resoldered with a new tin wall, using no flux in the soldering, which might partially penetrate into the interior of the reservoir, contaminating the liquid and depositing a gum which would interfere with the free fall of the weight. To facilitate soldering, the various parts which were to come in contact were previously tinned, using a flux in this preliminary tinning, because any excess could be readily wiped away. A weight of the dimensions judged to be most appropriate for the liquid under investigation was now selected, using as a criterion the known viscosity of the liquid at atmospheric pressure, and the apparatus was assembled by soldering in the plugs and the reservoir. During this assembly, which was made in a very bright light, preferably sunlight, the most rigorous scrutiny was made for minute particles of dirt, which were removed with the camel's hair brush.

The cylinder was now filled by exhausting as already described, and was then connected to the insulating plug which closes the pressure cylinder and was assembled into the pressure apparatus. This was usually done the last thing at night. In the morning a viscosity reading was made at once at the prevailing temperature of the room, which was 15° to 20°. The temperature of the bath was then raised to 30°, and after temperature equilibrium was reached another viscosity determination was made at atmospheric pressure. Pressure was now applied and a run made at 30° to 12000, or to the maximum pressure allowed by the freezing of the liquid. The freezing pressure was known in those cases in which the liquid had been previously investigated, but in a number of cases the freezing had not been previously investigated, and in the following will be found a number of new freezing points under pressure approximately determined. To have made an exact determination would have taken a great deal of time for the apparatus is not well adapted to this sort of measurement. Freezing is, of course, shown by the weight refusing to fall. There is no previous warning of the approach of freezing, but the viscosity curve of the liquid runs without change into the subcooled region. In the following the melting pressures are recorded as for example "freezes between 8000 and 10000 kg." or "melts between 7000 and 6000 kg." The first means that the substance was liquid at 8000 and on increasing pressure to 10000 it froze. The second means that at 7000 it was solid, and on releasing pressure to 6000 it melted. Because of the possibility of the supercooling of the liquid, the second method of determination is of course much the more accurate.

The number of pressure readings depended to some extent on the character of the liquid, more points being taken for a liquid whose viscosity changes rapidly with pressure or which could be measured over only a small range because of freezing. For those liquids which could be investigated over the entire pressure range of 12000 kg., readings were made at 0, 100, 500, 1000, 2000, 4000, 6000, 8000, 10000, and 12000 kg. If log viscosity is plotted against pressure a curve will be obtained nearly straight above 4000, but below this there is more or less curvature; this is the reason that the readings were multiplied at low rather than high pressures. In making the runs with the first few substances, pressure was released after the reading at the maximum of 12000, and check readings were made on the way down at 6000 and 0. There is no reason why a perfect check should not be obtained, unless the reservoir leaked or some

similar accident took place, because we are here dealing with the properties of a liquid which never have hysteresis. As a matter of fact, a perfect check was always obtained. The check readings having shown themselves unnecessary, in the case of the rest of the liquids, after the reading at 12000 and 30°, the temperature of the bath was changed to 75°, and the viscosity determined at 75° in decreasing pressure steps, retracing the steps of the ascending run to atmospheric pressure, if the boiling point of the liquid at atmospheric pressure was above 75°, or making the last reading at a pressure of a few atmospheres if the atmospheric boiling point was below 75°.

If the time of fall of the weight was less than 5 seconds, the time of 50 falls was taken, grouping the falls into five groups of ten. Above 5 seconds fall time, the mean of 10 fall times was taken, until the time got to be 40 or 50 seconds, when a smaller number of readings was taken, but never less than two even in the extreme case of one and a half hours. It has already been explained that the time of fall in the two directions might be slightly different because of lack of perfect symmetry in the two ends of the weight.

In the preliminary experiments a number of questions about the correct functioning of the apparatus were examined. In the first place it was established that the results could be repeated in that the apparatus could be taken apart and reassembled with the same liquid and the same readings obtained. If the falling weight was changed, either by changing the outside dimensions of the weight, or by putting a weight in the cavity keeping the outside dimensions the same, consistent results were obtained in that the ratio of the fall times at two different pressures was a constant.

Additional important checks are obtained by comparing the relative viscosities for different substances with those found by other observers. Nearly three-quarters of the readings were made with the same hollow weight, varying the total weight by the use of different cores. The relative times, corrected for the buoyancy of the liquid and the difference of total weight, of all these runs should be the same as the relative absolute viscosities determined by other observers. In Table I are given the corrected times of fall at 30° at atmospheric pressure, the absolute viscosity at 30° taken from the Smithsonian Tables, and the ratio of these two numbers for each liquid. The ratio should be constant, and the table shows that it is, except in one or two cases, with an error not greater than the usual discrepancy between viscosity determinations by different observers.

Another check is afforded by comparing the temperature coef-

ficient of viscosity at atmospheric pressure given by these experiments with the values of others. In Table II the ratio of the viscosity at 30° to that at 75° for some of the liquids of this investigation is compared with all the values given in the Smithsonian Tables for the same liquids. Again the agreement is satisfactory.

TABLE I.

Comparison of Relative Viscosities Obtained with the Pressure Apparatus with the Absolute Viscosities of Other Observers.

Liquid	Corrected Time of Fall at 30° (seconds)	Viscosity at 30° $\times 10^3$	$\frac{\text{Time}}{\text{Viscosity}} \times 10^3$
Ethyl Alcohol	10.4	1.003*	1.04
n-propyl Alcohol	17.4	1.779	.98
n-butyl Alcohol	22.2	2.24	.99
i-propyl Alcohol	17.2	1.757	.98
i-butyl Alcohol	28.9	2.864	1.01
n-pentane	2.17	.220	.99
n-hexane	2.79	.296	.94
n-octane	5.00	.483	1.04
i-pentane	2.18	.200	1.09
Ethyl Bromide	3.74	.368	1.02
Ethyl Iodide	5.52	.540	1.02
Ethyl Acetate	4.23	.407	1.04
CCl_4	8.65	.845	1.02
Chloroform	5.48	.519	1.06
CS_2	3.43	.352	.97
Ether	2.19	.223	.98
Benzene	5.72	.566	1.01
Toluene	5.53	.523	1.06
o-xylene	7.25	.709	1.02
m-xylene	5.92	.552	1.07
p-xylene	5.74	.568	1.01

The satisfactory functioning of the apparatus having been established, runs were made in the great majority of cases with only a single filling of the apparatus for a single substance.

It is not easy to estimate the probable accuracy of the relative

* The numbers in this column were obtained mostly from Smithsonian Tables or from Table III of this paper.

TABLE II.

COMPARISON OF TEMPERATURE COEFFICIENT OF VISCOSITY AT ATMOSPHERIC PRESSURE GIVEN BY THE PRESSURE APPARATUS WITH VALUES OF OTHER OBSERVERS.

Liquid	η_{30}/η_{75} Pressure Apparatus	Other Observers
Ethyl Alcohol	2.20	2.13*
n-propyl Alcohol	2.52	2.65
n-butyl Alcohol	2.84	2.81
i-propyl Alcohol	3.14	3.14
n-octane	1.55	1.58
Ethyl Iodide	1.46	1.44
CCl_4	1.74	1.69
Benzene	1.72	1.68
o-xylene	1.71	1.64
m-xylene	1.59	1.55
p-xylene	1.60	1.54
Toluene	1.60	1.56

viscosities under pressure yielded by these experiments. The maximum discrepancy in the time intervals was of the order of 0.5 seconds (10 intervals for fall times below 5 seconds, and single intervals above 5 seconds) giving a probable error in the averaged time of fall of something of the order of 0.05 second. The percentage error which this introduced into the final result depends on the total time of fall. As given in the following, the relative viscosities are the ratios of the corrected times of fall under the pressure and temperature in question to t_0, the corrected time of fall at atmospheric pressure at 30°. The percentage accuracy of these ratios obviously depends on the absolute value of t_0. In order to permit an estimate of this accuracy the value of t_0 is tabulated for each of the liquids. In Table V, to be given later, the logarithm to the base 10 of the relative viscosity is given as a function of pressure and temperature; one need expect no appreciable error in the shapes and relative positions of the log viscosity curves for times above 10 seconds. In addition to the accidental time errors, there may be consistent errors due to the various corrections; the more uncertain of the corrections are absolute and not percentage corrections, and so also are more important at the low

* Taken from Smithsonian Tables.

pressure end of the curves. Errors of this kind I believe to be considerably less than 0.01 seconds.

Some internal evidence as to probable accuracy is given by the closeness of the experimental points to a smooth curve. In constructing the table, the $\log_{10}$ of the corrected time of fall was plotted against pressure, smooth curves were drawn through the points, and the values at regular pressure intervals tabulated. The average numerical deviation from a smooth curve of $\log_{10}$ time is given in the table. The smoothness and self-consistency of the results was such that the theory of probable errors shows the justifiability of keeping more significant figures than are given here (logs to only three places are given), an uncertainty of 0.001 in the log corresponding to a percentage error of about 0.2%. The reason for not giving more significant figures was the very great increase of labor in computing the results which would have been involved. Three figures could be obtained fairly easily by direct graphical methods; another significant figure would have demanded computational methods at an enormous increase of time, which does not seem justified by any use which I can at present foresee will probably be made of these data.

In the case of water a great many experimental attempts were made, but an accuracy equal to that obtained with the other liquids was not achieved. The difficulty with water was caused by electrical conductivity of the water interfering with the operation of the timer through the electric contact arrangement. It was not possible to use the cylinder of bessemer steel used with the other liquids, because after the water had stood in contact with the steel for a while there was enough chemical action to produce a short-circuit in all positions of the weight. This was in spite of starting with water distilled in tin, from which all the air had been boiled out. Another viscosity cylinder was therefore made from one of the various grades of "rustless" iron recently put on the market. Considerable mechanical difficulty was found in machining this because of hard and soft spots, and the hole, although made as carefully as possible in the usual way with an ordinary reamer, was so much out of round as to introduce great irregularity, the weight falling freely in some positions, and in others sticking tight. A third apparatus was now made with another grade of rustless iron, this time the hole being *ground* true to within 0.00025 cm. To grind so long a hole as this to such an accuracy requires a high degree of mechanical skill, and I am much indebted to the firm of West and Dodge, who did the work. The falling weight was made of the same steel as the cylinder. But now

a great deal of trouble, not given by the first cylinder of rustless iron, was found with the electrical part of the apparatus; the apparatus would work perfectly in preliminary trials, but after running for a while the contact would fail. This was finally traced to the steel itself; after a number of sparks had passed between the cylinder and the weight a film was deposited of such highly insulating properties that it could not be broken down with any voltage feasible with the magneto. The steel of which the weight was formed was uneven in quality, and the contaminating film formed on the cap end in preference to the other. The difficulty was avoided at the low temperatures by making another cap of the original grade of rustless iron. With this, successful runs were made at 0° and 10°, but at 30° the insulation resistance became so great that the weight had to be discarded entirely, and a new one made of pure nickel. This worked well at 30°, but at 75° there was again trouble, both because of high insulation resistance to the falling weight, and electrolytic conductivity through the water. Only readings at pressures below 9000 were obtained at 75°, and these are in considerable doubt.

In reducing the readings to give correct relative viscosities over the entire range, correction had to be made for the change of weight between 10° and 30°. I made this correction so as to give between 10° and 30° the relative change of viscosity given by Bingham and Jackson.[6] For the relative changes between 0° and 10° and between 30° and 75°, the values given by these experiments were used. This gives a temperature coefficient of viscosity agreeing fairly well with that of Bingham between 30° and 75°, but materially larger between 0° and 10°.

Description of the Liquids.

There follows now a description of the various liquids used. These were obtained from various sources and were of varying degrees of purity. Fourteen of them were obtained through Professor J. Timmermans of the Bureau Belge d'Étalons Chimiques, for whose courtesy in providing me with the liquids I am much indebted; these were of an unusually high degree of purity. They were furnished in sealed glass tubes of approximately 10 cc. capacity. The tubes were not opened until immediately before filling the viscosity apparatus. The total time from breaking the glass seal to finally sealing the liquid into the viscosity apparatus was of the order of 5 minutes. Some of the physical constants of these liquids were determined by Professor Timmermans, and are given in the following table.

To Professor F. Keyes of the Mass. Institute of Technology I am indebted for CS_2, methyl and ethyl alcohol, ethyl ether, and normal pentane, also in sealed glass receptacles. These are also of a high degree of purity; the preparation and properties have been previously described by Professor Keyes.[7]

TABLE III.

PHYSICAL CONSTANTS OF LIQUIDS FROM BUREAU BELGE D'ETALONS CHIMIQUES.

Compound	Boiling Point	Densities 0°/4°	15°/4°	30°/4°	Viscosities×10⁵ 15°	30°
n-butyl alcohol	118°.10 (762 mm.)	0.8245	0.8134		3309	2237
n-amyl alcohol	137.27±.02 (751 mm.)	0.8395	0.8245			
i-pentane	27.95±.02	0.6393	0.62485			
Ethylene dibromide	132.00±.02		2.1911	2.1596	1880	1490
Ethyl acetate	77.15±.01	0.9245	0.9066			
n-butyl bromide	101.65±.02	1.3041	1.2830		626	537
CCl_4	75.75±.01	1.6326	1.6035		1040	845
Chloroform	61.20±.01	1.5264	1.49845			
n-amyl ether	185.26±.02 (750 mm.)	0.7990	0.7869			
Cyclohexane	80.75±.01		0.7830	0.7696	1056	828
Methyl cyclohexane	101.18±.01	0.7865	0.7734	0.7603	777	639
Benzene	80.15±.01		0.8841	0.8685	696	566
Chlorobenzene	132.00±.01	1.1280	1.1117	1.0954	844	711
Bromobenzene	156.15±.01	1.5200	1.5009		1196	985
Toluene	110.80±.01	0.88545	0.8716	0.8577	623	523
p-xylene	138.16±.01 (757 mm.)		0.8642	0.8526	682	568

The i-propyl alcohol I owe to Professor R. F. Brunel. This is from the same lot as that which I used previously in determining the effect of pressure on thermal conductivity. It was freshly distilled for this work in a Hempel column; and all came over at a temperature constant within 0.1°, the error of the thermometer.

Glycerine was Kahlbaum's purest, in a glass stoppered bottle.

The water was obtained from the Chemical Laboratory of Harvard University, and had been distilled in tin. There would have been no point in attempting to start with water of greater purity because of the impurities immediately absorbed by the water from the walls of the cylinder.

The other chemicals were obtained from the Eastman Kodak Co. and were of the best grades of those described in their catalogue of chemicals. The boiling points given in the catalogue for the liquids used here are reproduced.* In some cases the liquids were provided in glass stoppered bottles, but more often a cork stopper was used, separated from the liquid by a piece of paper. In such cases there was likely to be more or less mechanical dirt mixed with the liquid. Inclusion of any of this dirt in the viscosity apparatus was in almost all cases avoided by letting the bottle settle for some time, and then removing the liquid with a pipette, but in one or two cases an additional filtering was made through glass wool. Evidence of the purity of the liquid was in some cases obtained from the sharpness of freezing under pressure. If the liquid freezes sharply there are no pressures at which the weight will perceptibly leave one end of the cylinder (break contact), without falling completely to the other end, whereas if freezing is not sharp (liquid becomes mushy) the weight may break contact without falling completely to the other end.

Numerical Results.

The numerical results for all the substances except water are now given in Table V. The table gives $\log_{10}$ of the relative viscosity as a function of pressure and temperature, the viscosity at 30° and atmospheric pressure being taken as unity. The logarithm of the viscosity instead of the viscosity itself is given because the variation with pressure of the viscosity is very rapid, and the curve of viscosity against pressure has rapidly varying curvature, whereas the curve of log viscosity against pressure approaches a straight line at high pressure and is not too much curved at the low pressures. The pressures tabulated in the table are 0, 500, 1000, 2000, 4000, 6000, 8000, 10000, and 12000 kg./cm.^{2}, the intervals being shorter at the lower end of the range because of the much more rapidly varying curvature. From the values of the logarithms the ratio of the viscosity at atmospheric pressure at 30° to that at 75° may be found, and is tabulated. In the table are given the average numerical deviations from smooth curves of the observed logarithms. The deviation is usually not as much as 0.001 on the logarithm, and in general the observed points lay on a smooth curve within 0.1%. Since the accuracy of the time measurements depends on the absolute value of the time interval, the time of fall at 30° at atmospheric pressure (t_0) is given. For those substances with a relatively low value of t_0 the lower ends of the curves are relatively inaccurate, but there is

*See Table on p. 99.

TABLE V.

Substance		Pressure, kg./cm.² 1	500	1000	2000	4000	6000	8000	10000	12000	Average Deviation Smooth Curve	η_{30}	t_0	Wt.	Buoyancy Correction
Methyl Alcohol	$\log \frac{\eta}{\eta_0}$ 30°	.000	.094	.167	.286	.471	.616	.750	.874	.998	.001				.0048
	$\log \frac{\eta}{\eta_0}$ 75°	9.769	9.862	9.933	.043	.208	.334	.448	.555	.655	.001	.00520	1.73	B	.0130
	η_{30}/η_{75}	1.702	1.706	1.714	1.750	1.832	1.914	2.004	2.084	2.203				C	.0204
Ethyl Alcohol	$\log \frac{\eta}{\eta_0}$ 30°	.000	.107	.200	.363	.617	.829	1.023	1.211	1.390	.000				.0093
	$\log \frac{\eta}{\eta_0}$ 75°	9.657	9.772	9.873	.045	.289	.473	.634	.778	.919	.000	.01003	3.95	A	.0236
	η_{30}/η_{75}	2.203	2.163	2.123	2.080	2.128	2.270	2.449	2.710	2.958				E	.0359
n-propyl Alcohol	$\log \frac{\eta}{\eta_0}$ 30°	.000	.151	.283	.494	.836	1.131	1.402	1.667	1.915	.000				.0051
	$\log \frac{\eta}{\eta_0}$ 75°	9.598	9.754	9.880	.074	.368	.610	.827	1.033	1.223	.000	.01779	6.19	A	.0121
	η_{30}/η_{75}	2.523	2.495	2.529	2.630	2.938	3.319	3.758	4.305	4.920				C	.0179
n-butyl Alcohol	$\log \frac{\eta}{\eta_0}$ 30°	.000	.175	.321	.554	.934	1.289	1.609	1.912	2.208	.000				.004
	$\log \frac{\eta}{\eta_0}$ 75°	9.548	9.724	9.867	.089	.312	.690	.941	1.172	1.396	.000	.02237	2.90	A	.010
	η_{30}/η_{75}	2.845	2.838	2.858	2.932	3.343	3.991	4.679	5.521	6.518				D	.015
n-amyl Alcohol	$\log \frac{\eta}{\eta_0}$ 30°	.000	.188	.341	.607	1.060	1.448	1.811	2.164	2.495	.000				.0087
	$\log \frac{\eta}{\eta_0}$ 75°	9.540	9.723	9.871	.105	.466	.772	1.049	1.313	1.562	.000		2.29	F	.0212
	η_{30}/η_{75}	2.884	2.917	2.951	3.177	3.926	4.742	5.781	7.096	8.570					.0320
i-propyl Alcohol	$\log \frac{\eta}{\eta_0}$ 30°	.000	.193	.343	.591	.982	1.318	1.640	1.977	2.311	.000				.004
	$\log \frac{\eta}{\eta_0}$ 75°	9.505	9.695	9.851	.087	.425	.701	.957	1.191	1.424	.002	.01757	2.24	A	.011
	η_{30}/η_{75}	3.141	3.164	3.120	3.208	3.624	4.161	4.844	6.140	7.748				D	.015
i-butyl Alcohol	$\log \frac{\eta}{\eta_0}$ 30°	.000	.210	.388	.696	1.203	1.655	2.075	2.483	2.898	.000				.0042
	$\log \frac{\eta}{\eta_0}$ 75°	9.444	9.659	9.824	.075	.488	.838	1.158	1.459	1.747	.000	.02864	3.78	A	.0103
	η_{30}/η_{75}	3.597	3.556	3.664	4.178	5.188	6.561	8.260	10.57	14.16				D	.0153

TABLE V.—*Continued.*

Substance		Pressure, kg./cm.² 1	500	1000	2000	4000	6000	8000	10000	12000	Average Deviation Smooth Curve	η_{30}	l_0	Wt.	Buoyancy Correction
i-amyl Alcohol	$\log \frac{\eta}{\eta_0}$ 30°	.000	.209	.386	.686	1.185	1.636	2.069	2.505	2.952	.000				.0087
	$\log \frac{\eta}{\eta_0}$ 75°	9.424	9.618	9.787	.065	.492	.848	1.168	1.483	1.780	.000		.70	G	.0211
	η_{30}/η_{75}	3.805	3.939	4.012	4.221	4.970	6.200	8.042	11.41	15.76					.0316
n-pentane	$\log \frac{\eta}{\eta_0}$ 30°	.000	.181	.315	.524	.847	1.112	1.360	1.615	1.846	.002				.011
	$\log \frac{\eta}{\eta_0}$ 75°	9.811	.014	.163	.380	.676	.908	1.119	1.313	1.493	.000	.00220	2.32	A	.027
	η_{30}/η_{75}	1.545	1.469	1.419	1.393	1.483	1.600	1.742	2.004	2.254					.040
n-hexane	$\log \frac{\eta}{\eta_0}$ 30°	.000	.184	.332	.561	.914	1.224	1.514	1.803		.001				.0105
	$\log \frac{\eta}{\eta_0}$ 75°	9.803	.028	.171	.379	.701	.961	1.198	1.426	1.646	.000	.00296	2.99	A	.027
	η_{30}/η_{75}	1.574	1.432	1.449	1.521	1.633	1.832	2.070	2.382						.040
n-octane	$\log \frac{\eta}{\eta_0}$ 30°	.000	.196	.327	.641	1.088	1.487				.000			A	.0043
	$\log \frac{\eta}{\eta_0}$ 75°	9.810	.003	.153	.390	.763	1.080	1.363	1.630		.000	.00483	1.75	C	.0119
	η_{30}/η_{75}	1.549	1.560	1.493	1.782	2.113	2.553								.0144
i-pentane	$\log \frac{\eta}{\eta_0}$ 30°	.000	.202	.344	.559	.894	1.175	1.431	1.687	1.947	.000				.0101
	$\log \frac{\eta}{\eta_0}$ 75°	9.821	.040	.193	.408	.715	.960	1.179	1.381	1.586	.000	.00198	2.34	A	.0258
	η_{30}/η_{75}	1.510	1.452	1.416	1.416	1.510	1.641	1.786	2.023	2.296					.0398
i-amyl Decane	$\log \frac{\eta}{\eta_0}$ 30°	.000	.237	.435	.772	1.354					.001			A	.0084
	$\log \frac{\eta}{\eta_0}$ 75°	9.772	9.989	.178	.463	.925	1.334	1.727			.000		2.65	E	.0210
	η_{30}/η_{75}	1.690	1.770	1.807	2.037	2.685									.0319
Ethylene Di-bromide	$\log \frac{\eta}{\eta_0}$ 30°	.000	.138								.001				.0296
	$\log \frac{\eta}{\eta_0}$ 75°	9.756	9.885	.003	.203	.354					.000	.01490	20.6	A	.0739
						(3000)					1 discard				
	η_{30}/η_{75}	1.754	1.791												.0837

TABLE V.—*Continued.*

Substance		Pressure, kg./cm.² 1	500	1000	2000	4000	6000	8000	10000	12000	Average Deviation Smooth Curve	η_{30}	t_0	Wt.	Buoyancy Correction
Ethyl Chloride	$\log \frac{\eta}{\eta_0}$ 30°	.000	.134	.242	.405	.649	.837	1.008	1.172	1.323	.001				.0150
	$\log \frac{\eta}{\eta_0}$ 75°	9.850	.017	.131	.285	.514	.683	.834	.977	1.111	.000		2.54	A	.0341
	η_{30}/η_{75}	1.413	1.309	1.291	1.318	1.365	1.426	1.493	1.567	1.633					.0443
Ethyl Bromide	$\log \frac{\eta}{\eta_0}$ 30°	.000	.121	.222	.387	.631	.854	1.043	1.223	1.400	.000				.0195
	$\log \frac{\eta}{\eta_0}$ 75°	9.806	9.959	.072	.235	.472	.653	.816	.978	1.123	.000	.00368	4.54	A	.0486
	η_{30}/η_{75}	1.567	1.452	1.413	1.419	1.442	1.589	1.687	1.758	1.892					.0602
Ethyl Iodide	$\log \frac{\eta}{\eta_0}$ 30°	.000	.115	.218	.385	.656	.888	1.108	1.330	1.549	.001				.0144
	$\log \frac{\eta}{\eta_0}$ 75°	9.837	9.954	.057	.227	.467	.672	.854	1.030	1.200	.004	.00540	2.15	A C	.0363
	η_{30}/η_{75}	1.455	1.449	1.445	1.439	1.545	1.644	1.795	1.995	2.234					.0551
Acetone	$\log \frac{\eta}{\eta_0}$ 30°	.000	.135	.226	.373	.605	.804	.987	1.160		.000				.0051
	$\log \frac{\eta}{\eta_0}$ 75°	9.895	.017	.113	.245	.445	.610	.762	.898	1.031	.002	.00285	1.16	A C	.0139
	η_{30}/η_{75}	1.274	1.312	1.297	1.343	1.445	1.563	1.679	1.828						.0213
Glycerine	$\log \frac{\eta}{\eta_0}$ 30°	.000	.134	.260	.497	.936	1.346	1.741	2.133		.000				.0088
	$\log \frac{\eta}{\eta_0}$ 75°	8.810	8.920	9.023	9.204	9.529	9.818	.094	.369	.628	.001	3.8	9.42	H	.0186
	η_{30}/η_{75}	15.49	16.37	17.26	19.63	25.53	33.73	44.36	58.08						.0291
Ethyl Acetate	$\log \frac{\eta}{\eta_0}$ 30°	.000	.142	.258	.463	.818	1.120	1.393	1.686	1.974	.003				.0060
	$\log \frac{\eta}{\eta_0}$ 75°	9.836	9.976	.081	.253	.517	.761	.992	1.213	1.416	.000	.0039	1.50	A C	.0151
	η_{30}/η_{75}	1.459	1.466	1.503	1.622	2.000	2.286	2.518	2.972	3.614					.0229
n-butyl Bromide	$\log \frac{\eta}{\eta_0}$ 30°	.000	.143	.269	.474	.816	1.115	1.408	1.715	2.018	.000				.0088
	$\log \frac{\eta}{\eta_0}$ 75°	9.832	9.975	.090	.273	.564	.811	1.040	1.264	1.484	.002	.00537	2.21	A C	.0214
	η_{30}/η_{75}	1.472	1.472	1.510	1.589	1.786	2.014	2.333	2.825	3.420					.0319

TABLE V.—*Continued.*

Substance		Pressure, kg./cm.² 1	500	1000	2000	4000	6000	8000	10000	12000	Average Deviation Smooth Curve	η_{30}	t_0	Wt.	Buoyancy Correction
Cineole	$\log \frac{\eta}{\eta_0}$ 30°	.000	.315								.002				.0099
	75°	9.654	9.905	.142	.575						.000		2.03	F	.0241
	η_{30}/η_{75}	2.218	2.570												.0364
Oleic Acid	$\log \frac{\eta}{\eta_0}$ 30°	.000	.306	.616							.000				.0103
	75°	9.419	9.671	9.989	.255	.843					.001		2.72	I	.0265
	η_{30}/η_{75}	3.811	4.315	4.236											.0402
CCl_4	$\log \frac{\eta}{\eta_0}$ 30°	.000	.190	.351	.493 (1500)						.000			A	.0095
	75°	9.760	9.949	.100	.349	.542					.002	.00845	3.26	C	.0267
	η_{30}/η_{75}	1.738	1.742	1.782											.0529
Chloroform	$\log \frac{\eta}{\eta_0}$ 30°	.000	.110	.211	.386	.660	.884				.002			A	.0104
	75°	9.858	9.985	.094	.251	.480	.691	.914	1.141		.000	.00519	2.05	C	.0261
	η_{30}/η_{75}	1.387	1.334	1.309	1.365	1.514	1.560								.0396
CS_2	$\log \frac{\eta}{\eta_0}$ 30°	.000	.090	.160	.307	.509	.674	.840	1.010	1.189	.002				.0133
	75°	9.875	9.972	.051	.180	.372	.527	.671	.808	.946	.000	.00352	4.05	A	.0375
	η_{30}/η_{75}	1.334	1.312	1.285	1.340	1.371	1.403	1.476	1.592	1.750					.0491
Ether	$\log \frac{\eta}{\eta_0}$ 30°	.000	.189	.324	.514	.792	1.042	1.261	1.469	1.670	.002				.0109
	75°	9.878	.024	.149	.344	.601	.806	.986	1.155	1.311	.000	.00212	2.38	A	.0258
	η_{30}/η_{75}	1.324	1.462	1.496	1.479	1.552	1.722	1.884	2.061	2.286					.0398
n-amyl Ether	$\log \frac{\eta}{\eta_0}$ 30°	.000	.218	.401	.708	1.230	1.685	2.091			.002			A	.0048
	75°	9.736	9.943	.107	.364	.776	1.125	1.437	1.728	2.007	.000		3.44	C	.0114
	η_{30}/η_{75}	1.837	1.884	1.968	2.208	2.844	3.631	4.508							.0169

TABLE V.—*Continued.*

Substance		Pressure, kg./cm.² 1	500	1000	2000	4000	6000	8000	10000	12000	Average Deviation Smooth Curve	η_{30}	t_0	Wt.	Buoyancy Correction
Cyclohexane	$\log \frac{\eta}{\eta_0}$ 30°	.000	.261								.000				.0063
	75°	9.723	9.975	.169	.341 (1500)						.002	.00828	9.18	A	.0169
	η_{30}/η_{75}	1.892	1.932												
Methyl Cyclohexane	$\log \frac{\eta}{\eta_0}$ 30°	.000	.220	.388	.710	1.274	1.804	2.318			.003				.0037
	75°	9.747	9.976	.154	.434	.900	1.335	1.756	2.167	2.582	.000	.00639	2.14	B C	.0100
	η_{30}/η_{75}	1.791	1.754	1.714	1.888	2.366	2.944	3.648							.0163
Benzene	$\log \frac{\eta}{\eta_0}$ 30°	.000	.173	.347							.001				.0087
	75°	9.765	9.938	.081	.308	.498 (3000)					.003	.00566	6.34	A	.0202
	η_{30}/η_{75}	1.718	1.718	1.845											
Chlorobenzene	$\log \frac{\eta}{\eta_0}$ 30°	.000	.133	.253	.478	.867	1.223				.002				.0099
	75°	9.814	9.936	.053	.245	.563	.852	1.146	1.465		.000	.00711	2.38	B C	.0208
	η_{30}/η_{75}	1.535	1.574	1.585	1.710	2.014	2.350								.0312
Bromobenzene	$\log \frac{\eta}{\eta_0}$ 30°	.000	.138	.262	.486	.897					.000				.0099
	75°	9.801	9.930	.044	.228	.558	.874	1.029 (7000)			.000	.00985	3.29	A C	.0234
	η_{30}/η_{75}	1.581	1.614	1.652	1.811	2.183									.0346
Aniline	$\log \frac{\eta}{\eta_0}$ 30°	.000	.195	.376	.709						.001				.0037
	75°	9.551	9.703	9.847	.102	.560					.000	.0319	4.08	A D	.0101
	η_{30}/η_{75}	2.812	3.105	3.381	4.046										.0162

TABLE V.—*Continued.*

Substance		Pressure, kg./cm.² 1	500	1000	2000	4000	6000	8000	10000	12000	Average Deviation Smooth Curve	η_{30}	t_0	Wt.	Buoyancy Correction
Diethyl-aniline	$\log \frac{\eta}{\eta_0}$ 30°	.000	.201	.394	.761	1.070 (3000)					.002				.0110
	75°	9.690	9.839	9.984	.259	.758	1.250	1.775			.003		1.32	F	.0279
	η_{30}/η_{75}	2.042	2.301	2.570	3.177										.0424
Nitro-benzene	$\log \frac{\eta}{\eta_0}$ 30°	.000	.134	.264							.001		2.23	A D	.0045
	75°	Decomposes													.0121
	η_{30}/η_{75}														.0194
Toluene	$\log \frac{\eta}{\eta_0}$ 30°	.000	.145	.274	.497	.897	1.285	1.699	2.177		.000			A	.0049
	75°	9.796	9.939	.065	.267	.597	.896	1.186	1.504	1.832	.000	.00523	1.96	C	.0137
	η_{30}/η_{75}	1.600	1.607	1.618	1.698	1.995	2.449	3.258	4.710						.0213
o-xylene	$\log \frac{\eta}{\eta_0}$ 30°	.000	.165	.311	.577						.000			A	.0054
	75°	9.767	9.925	.057	.292	.689	1.087				.001	.00709	2.57	C	.0131
	η_{30}/η_{75}	1.710	1.738	1.795	1.928										.0196
m-xylene	$\log \frac{\eta}{\eta_0}$ 30°	.000	.154	.290	.529	.967					.001				.0092
	75°	9.799	9.959	.079	.286	.637	.983	1.333			.001	.00552	6.55	A	.0226
	η_{30}/η_{75}	1.589	1.567	1.626	1.750	2.138									.0336
p-xylene	$\log \frac{\eta}{\eta_0}$ 30°	.000	.152								.000			A	.0054
	75°	9.797	9.957	.092	.315						.003	.00568	2.04	C	.0130
	η_{30}/η_{75}	1.596	1.567												.0196
p-cymene	$\log \frac{\eta}{\eta_0}$ 30°	.000	.172	.333	.626	1.194	1.859				.000			B	.0059
	75°	9.800	9.948	.087	.335	.749	1.168	1.612	2.164		.000		2.43	C	.0149
	η_{30}/η_{75}	1.585	1.675	1.762	1.954	2.786	4.977								.0226

TABLE V.—*Continued.*

Substance	Pressure, kg./cm.² 1	500	1000	2000	4000	6000	8000	10000	12000	Average Deviation Smooth Curve	η_{30}	t_0	Wt.	Buoyancy Correction
Eugenol $\log \frac{\eta}{\eta_0}$ 30°	.000	.288	.541	1.081	2.273	3.007				.003				.0138
				1.652	(3000)	(5000)								
75°	9.429	9.616	9.810	.143	.805	1.520	2.343			.001		1.70	G	.0326
η_{30}/η_{75}	3.724	4.699	5.383	8.670	29.38									.0496
Petroleum Ether $\log \frac{\eta}{\eta_0}$ 30°	.00	.16	.30	.54	.93	1.28	1.59	1.88	2.18					
80°					.56	.83	1.06	1.28	1.49			2.75		(*)
η_{30}/η_{80}					2.34	2.82	3.39	3.98	4.90					
Kerosene $\log \frac{\eta}{\eta_0}$ 30°	.00	.24	.46	.88	1.71									
80°					.91	1.41	1.88	2.34	2.80			3.80		(*)
η_{30}/η_{80}					6.3									

(*) No buoyancy correction applied.

Designation of Weights

A 1.014 gm. Fe	D 7.041 gm. Au	G 3.821 gm. Fe
B .997 gm. Fe	E 1.921 gm. Fe	H 3.134 gm. Fe
C 2.008 gm. W	F 4.108 gm. Fe	I 3.470 gm. Fe

no error arising from this source in the relative values at the higher pressures. The falling weights are tabulated and in the last column the corrections assumed for the buoyancy of the liquid at 2000, 6000, and 12000 kg., respectively. For those liquids whose compressibility has not been directly measured a small correction may have to be made at some future time when the compressibility is measured, permitting a more accurate buoyancy correction. Also, for convenience in the discussion, the absolute viscosities at atmospheric pressure at 30° are listed when these are known; many of these values were taken from the Smithsonian Tables, and others were given by Timmermans.

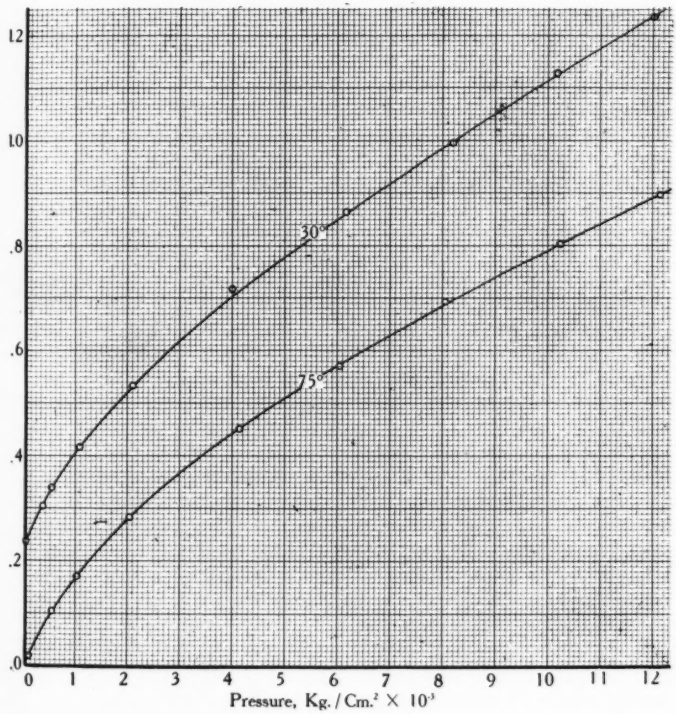

FIGURE 3. The common logarithm of the corrected time of fall of the weight against pressure for methyl alcohol. The time of fall is proportional to viscosity.

Sample curves for two substances, giving observed logarithm of the relative viscosity, are shown in Figures 3 and 4.

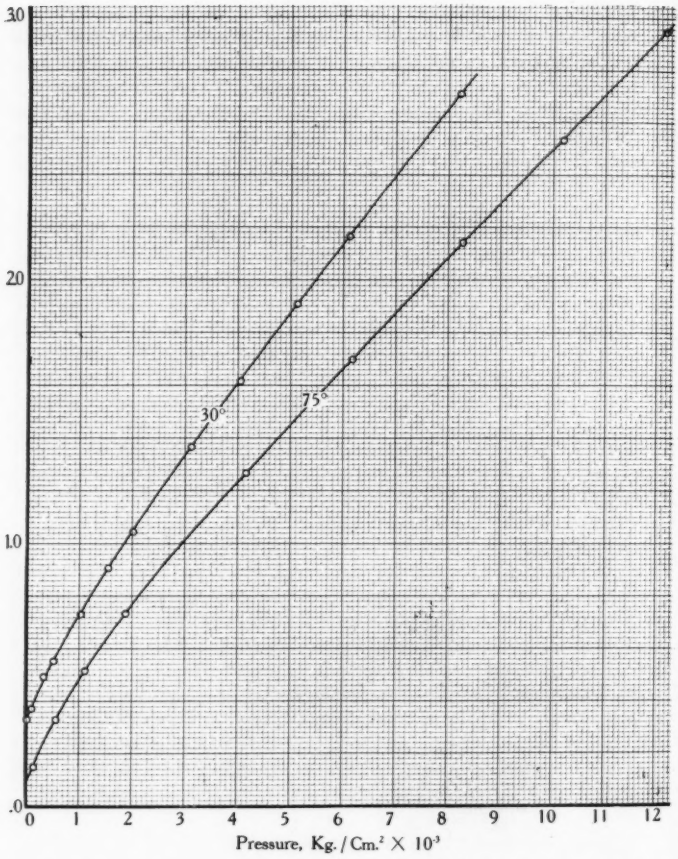

FIGURE 4. The common logarithm of the corrected time of fall of the weight against pressure for methyl-cyclohexane. The time of fall is proportional to viscosity.

Because of its comparatively small variation of viscosity with pressure, water is treated separately. In Table VI. are given the

relative viscosities (not log relative viscosity) as a function of pressure at 0°, 10°, 30°, and 75°. The pressure range at the two lowest temperatures was terminated by freezing, and at 75° the limit was set by the experimental difficulties already described. The experimental points are plotted in Figure 5. The experimental irregularity is much greater than for the other liquids which are better insulators, but still is not great enough to leave any doubt as to the essential character of the facts.

TABLE VI.

RELATIVE VISCOSITY OF WATER.

Pressure kg./cm.²	Relative Viscosity			
	0°	10.3°	30°	75°
1	1.000	.779	.488	.222
500	.938	.755	.500	.230
1000	.921	.743	.514	.239
1500	.932	.745	.530	.247
2000	.957	.754	.550	.258
3000	1.024	.791	.599	.278
4000	1.111	.842	.658	.302
5000	1.218	.908	.720	.333
6000	1.347	.981	.786	.367
7000		1.064	.854	.404
8000		1.152	.923	.445
9000			.989	.494
10000			1.058	
11000			1.126	

Some of the liquids require special comment.

Methyl Alcohol. Two attempts were necessary with this. At first a portion of the same sample was used as had been used for the thermal conductivity measurements under pressure. This had been sealed in glass since extracting the thermal conductivity sample, but nevertheless had absorbed sufficient moisture from the air during that brief handling to make it so conducting that the method failed. A second fresh sample was obtained from Professor Keyes, also prepared in 1923, but sealed in glass ever since. This was a sufficiently good insulator to give good readings.

Ethyl Alcohol. At 75°, at a pressure of 2000 kg. and below, the electrical conductivity became so great that the electrical timing

device ceased to function, and a telephone and stop-watch had to be substituted. This gives less accurate results, the smallest division of the stop-watch being 0.2 seconds, so that the lower end of the 75° is much more in error than usual. The upper end of the 75° curve is not affected by this error, neither is any part of the 30° curve.

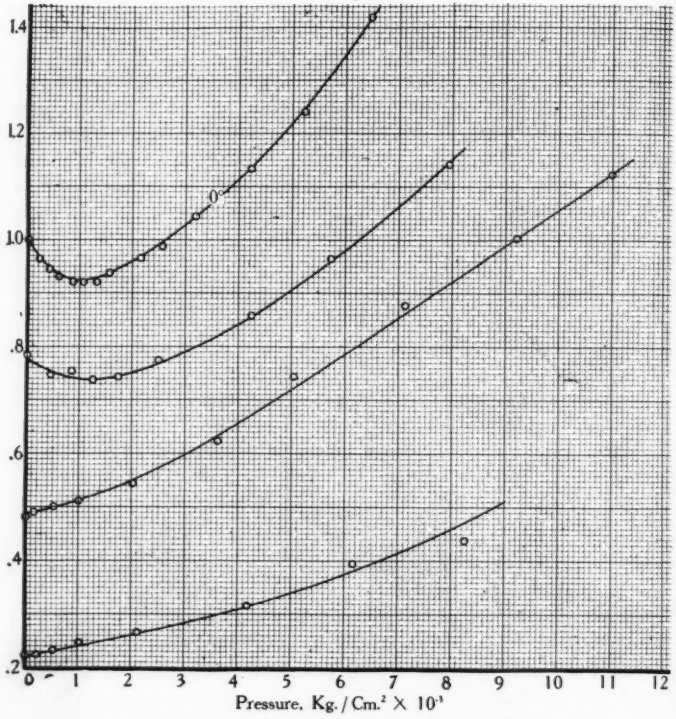

FIGURE 5. The relative viscosity of water at 0°, 10°, 30°, and 75° as a function of pressure.

i-Butyl Alcohol. Two fillings were necessary, the connecting pipe to the pressure generating apparatus having split on the first application of 10000 kg. at 30°. The second filling gave all the points at 75°, and the points at 10000 and 12000 at 30°, and several check points at lower pressures, which agreed within 0.1%.

n-Octane. Two fillings were necessary; after a number of readings at 30°, the weight stuck because of mechanical dirt. A heavier weight was used with the second filling. The results of the two fillings agreed after correction for the difference of weight.

Ethyl Chloride. The boiling point at atmospheric pressure is about 12°. The experiment was done in winter; during the filling of the apparatus the room was cooled to 0° C. by opening the windows.

Acetone. This was cleaned from mechanical dirt before filling the apparatus by filtering through glass wool.

Ethyl Ether. Two fillings of the apparatus was necessary, the weight sticking because of mechanical dirt after the run at 30°. A check reading was made at 30° with the second filling, agreeing within a few thousandths of a second.

Nitro Benzene. Readings were obtained only at 30°. At 75°, at 1200 kg., the liquid short circuited, as it did also at 2200. The apparatus was then taken apart, and the nitro benzene found completely decomposed, with a heavy deposit of lamp black.

Incidental Data.

In addition to the viscosity, a certain amount of incidental data was also obtained, as already mentioned. The approximate values of the freezing pressures are collected in Table VII.

The compressibility of glycerine was also determined approximately. This was done by a new method, which is to be applied in the future to a large number of liquids, and will be described in detail then. Briefly, the liquid is placed in a piezometer with freely moving piston, and immersed in the liquid by which pressure is transmitted. Under pressure, the piston moves in, equalizing pressure inside and out, and the motion of the piston is measured by a sliding wire scheme with potentiometer contacts much like the lever arrangement for measuring compressibility. Since the compressibility of glycerine was needed only in a correction term, no attempt was made to apply all the corrections in working up the results, and in Table VIII the change of volume at 30° is tabulated as a function of pressure to only two significant figures. The particular interest of this substance, glycerine, lies in its extremely low compressibility for a non-metallic substance.

Comparison with Previous Results.

For comparison there are practically only the results of Faust[1] to 3000 kg. on ethyl alcohol, ether, and CS_2. He finds for ethyl

alcohol an increase of viscosity at 30° under 3000 kg. of 2.94 fold against my 2.31, for ether 3.96 fold against my 3.27, and for CS_2 3.43 against 2.03. The agreement certainly ought to be much closer. Faust used a flow method through a glass capillary under a varying head of mercury. It is not evident from his paper whether all the corrections were applied, but it is hard to see how any corrections could be responsible for so large a difference.

TABLE VII.

ROUGH FREEZING DATA UNDER PRESSURE.

Substance	Freezing Data	
	30°	75°
n-hexane	10600 kg./cm.²	
n-octane	6100	10000
i-amyl Decane	Freezes between 4000 and 6100	Melts between 8200 and 7130
Ethylene Dibromide	Freezes between 600 and 800	Freezes between 2500 and 2800
Cineole	Freezes between 900 and 1000	Freezes between 2100 and 2500
Oleic Acid	Freezes between 100 and 1600	Melts below 5000
n-amyl ether	Freezes between 8200 and 9500	
Cyclohexane	Freezes between 400 and 500	Freezes between 1400 and 1600
Methyl Cyclohexane	Freezes between 8000 and 10000	
Diethyl Aniline	Melts between 3000 and 2600	Freezes between 7200 and 7800*
o-xylene	2400	5500
m-xylene	4000	above 5200
p-xylene	490	1900

GENERAL CHARACTER OF THE RESULTS.

In certain qualitative features, the behavior of all the liquids investigated here, except water, is alike, although there are very large quantitative differences. The viscosity increases with pressure at a rapidly increasing rate, so that if viscosity is plotted against pressure a curve of very rapid upward curvature is obtained. This is unusual;

TABLE VIII.

COMPRESSIBILITY OF GLYCERINE.

Pressure kg./cm.²	$\frac{\Delta V}{V_0}$ at 30°	Pressure kg./cm.²	$\frac{\Delta V}{V_0}$ at 30°
2000	.042	8000	.107
4000	.068	10000	.121
6000	.089	12000	.134

most pressure effects become relatively less at high pressure by a sort of law of diminishing returns. In Figure 6 is shown viscosity against

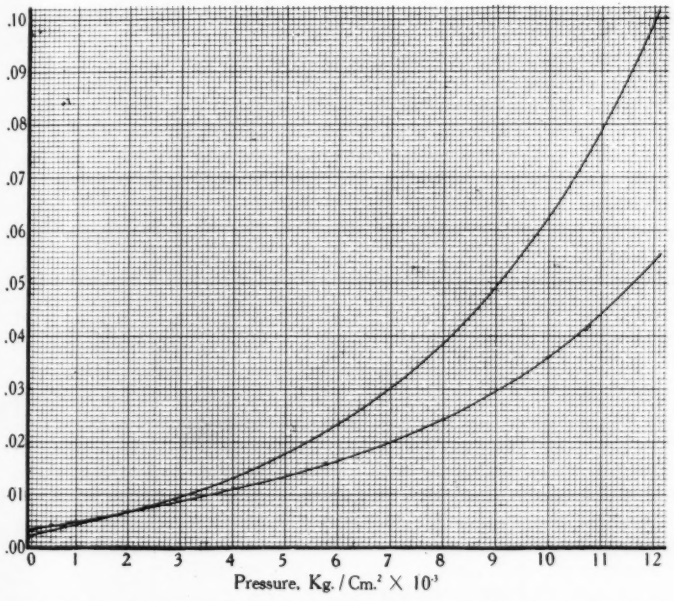

FIGURE 6. The viscosity in Abs C.G.S. units at 30° C. of CS_2 and ether as a function of pressure. The curve for ether starts below that for CS_2 and rises above it beyond 2000 kg.

pressure at 30° for CS_2 and ether, two substances with comparatively small pressure effect. It is seen that over the first two or three thou-

sand kilograms the relation between pressure and viscosity is nearly linear, but above this the departure is extreme. If logarithm viscosity is plotted against pressure a curve is obtained in general concave toward the pressure axis. The curvature is much the greatest at low pressures; above 2000 or 3000 kg. the curve approximates to a straight line, or indeed in a number of cases reverses curvature. This means that above 3000 viscosity increases approximately geometrically as pressure increases arithmetically.

A number of substances show reverse curvature, log viscosity being convex toward the pressure axis at high pressures, which means that viscosity increases more rapidly than geometrically when pressure increases arithmetically. Eugenol and p-cymene show the effect more markedly than do any other substances. The following list

TABLE IX.

LIST OF SUBSTANCES FOR WHICH LOG η IS CONVEX TO PRESSURE AXIS AT HIGH PRESSURES.

Substance	Temperature	
i-propyl Alcohol	30°	
i-butyl Alcohol	30°	
i-amyl Alcohol	30°	
i-pentane	30°	75°
Ethyl Acetate	30°	
n-butyl Bromide	30°	75°
Chloroform		75°
CS_2	30°	75°
Methyl Cyclohexane	30°	75°
Chlorobenzene		75°
Diethyl Aniline		75°
Toluene	30°	75°
o-xylene		75°
m-xylene	30°	75°
p-cymene	30°	75°
Eugenol	30°	75°
Petroleum Ether	30°	

contains those substances for which this effect seems certain beyond experimental error.

The temperature coefficient of viscosity is shown by the rows in Table V. giving η_{30}/η_{75}. Here again the effect is abnormal; most

temperature effects become less at high pressures, which is to be expected if the modification in the structure produced by temperature agitation becomes less under the greater constraints imposed by the high pressure. But here the relative change of viscosity with temperature becomes very markedly greater at high pressure, the ratio η_{30}/η_{75} changing under 12000 kg. by a factor of as much as 4.

Apart from these qualitative resemblances, the most varied quantitative behavior is shown by the various substances. In fact, viscosity is a unique property in regard to the magnitude of the pressure effect and its variation from substance to substance. The compressibility at atmospheric pressure, for example, varies by a factor of not more than four or five fold for the substances investigated here, and under 12000 kg. the compressibility of any one substance diminishes by not over 15 fold. The thermal expansion changes by a factor of two or three under 12000 for these liquids, and the specific heats and thermal conductivities do not vary more. Excepting water, the smallest effect of pressure on viscosity found above is that on methyl alcohol, which increases 10 fold under 12000, and the largest is by over 10^7 for eugenol (obtained by linear extrapolation, which gives too low a value).

In general the largest pressure effects are for those substances with the most complicated molecules. This is very plainly shown by the series of the alcohols, or by the various compounds derived from benzene; the relative pressure effect is greater the more complicated the group substituted for hydrogen. There is also a very marked constitutive effect, the iso-compounds having a larger effect than the normal compounds, and a similar effect is seen in the three xylenes. A heavier atom substituted into a molecule produces in general a larger pressure effect, as is shown in the series C_2H_5Cl, $-Br$, $-I$. or by chloro- and bromo-benzene. There appears, however, to be a tendency working in the other direction at low pressures. In the ethyl halogen series, the increase of viscosity produced by 500 kg. is in the order Cl, Br, I, whereas the increase under 12000 is in the order I, Br, Cl. It may well be that the abnormal effect at low pressure is due to the abnormally large compressibility of C_2H_5Cl, due to the neighborhood of the critical point, at which the compressibility is infinite. Abnormal behavior is also shown by methyl cyclohexane, the pressure effect being larger than for cyclohexane.

Water is quite different in character from the other liquids. Previous investigations have been made to 400 kg. by Hauser.[1] He

found that, below 30°, viscosity decreases with increasing pressure, and above 30°, increases. At higher pressures we now find that at 0° and 10° there is a minimum viscosity, at a pressure roughly 1000 kg., the minimum being less pronounced at 10° than at 0°. At 30° and 75° there is a regular increase of viscosity with pressure over the entire range. (Not much weight must be placed on the precise numerical values given for 75°, there being much experimental uncertainty here because of electrical conductivity by the water.) It is natural to see in this abnormal behavior of water an association effect; at low pressures and temperatures, water is strongly associated with large molecules and a large viscosity, but as pressure increases the association decreases, and the average size of the molecules decreases, giving a term in the viscosity which diminishes fast enough to more than compensate the normal increase of viscosity under pressure. At higher pressures the association effect is exhausted, and the behavior becomes normal.

Theoretical Discussion.

It is generally recognized that the mechanism of viscosity is very different in a gas and a liquid. In a gas, viscosity increases with rising temperature, and is constant with increasing pressure, whereas in a liquid, viscosity decreases with rising temperature and increases with rising pressure. A further essential difference is shown by the connection between viscosity and thermal conductivity. In a gas, momentum and energy are conveyed by the same mechanism, so that reciprocal viscosity and thermal conductivity are proportional, whereas in a liquid the mechanisms are different, as is shown by the increase of thermal conductivity with increasing pressure and the very great decrease of reciprocal viscosity.

The mechanism of viscosity and thermal conductivity is well understood for a gas, but we have little understanding of the mechanism for a liquid, and there have been few attempts at theoretical explanation. In the following I shall not attempt to offer a theory of liquid viscosity, but shall try to show that the pressure phenomena make it pretty evident that there is a very important element in liquid viscosity which has been overlooked in previous theoretical attempts.

The few theoretical discussions of liquid viscosity have attached especial significance to the relation between viscosity and volume. Faust[1] drew from his measurements the conclusion that at high pressures viscosity tends to a limiting behavior, in which it is a linear

function of the volume only, so that the viscosity is constant at a given volume independent of temperature (pressure varying). This behavior he found for CS_2 and ether in the pressure range of 3000 kg., but he found that ethyl alcohol did not approach such a behavior. The new data of this paper show that at high pressures the viscosity of all substances departs very far indeed from being a linear function of volume at a definite temperature, or from being a pure volume function of any kind. Faust saw a connection between the supposed linear relation between volume and viscosity and Tammann's theory that in the domain of high pressures the forces of molecular attraction are constant.

The most elaborate of the theories of liquid viscosity is that of L. Brillouin,[8] whose guiding idea is that part of the viscosity arises from a transfer of momentum through the liquid by elastic waves, in much the same way as Debye has a thermal conduction (energy transfer) by elastic waves. The mathematical working out of the idea is elaborate and reference must be made to the original paper; the important result is found that the dissipation of the continuity of the waves by temperature agitation produces a viscosity decreasing with rising temperature. No formula is given for the effect of pressure on viscosity at constant temperature, and indeed the theory must be extended to be capable of giving such a formula, but an exact expression is found for the change of viscosity with temperature at constant volume. The expression is:

$$\left(\frac{\partial \eta}{\partial \tau}\right)_v = -\frac{5}{3}\frac{\chi}{V^2},$$

where χ is the thermal conductivity in absolute mechanical units and V is the velocity of sound. The value for the temperature coefficient of viscosity at constant volume given by the formula turns out to be about 100 times smaller than the coefficient as ordinarily measured at constant pressure (atmospheric). Brillouin tried to get an exact numerical check of his expression for $(\partial\eta/\partial\tau)_v$ from the data of Faust, and drew the conclusion that there was agreement within experimental error, which, however, he admitted might be very large.

The new data of this paper are sufficiently accurate to allow a check of the formula. It turns out that the formula fails by so large a factor as to constitute another order of magnitude. Thus for ether at a volume of 0.80 my value of viscosity at 30° and 75° gives

$$\left(\frac{\partial \eta}{\partial \tau}\right)_v = -.00106,$$

against a value of $(5/3)(\chi/V^2)$ of

$$2.18 \times 10^{-7}\left[=\frac{5}{3}\times\frac{1.38\times 10^4}{(3.24)^2\times 10^{10}}\right].$$

The values of χ, V, and volume involved in this calculation were taken from previous papers on compressibility and thermal conductivity.[3, 4] The difference between the calculated and observed value is so great that experimental error seems absolutely incapable of explaining it.

Another theory of viscosity has been developed by Phillips,[9] who has momentum transferred from part to part of the liquid by a quantum mechanism. He draws the conclusion that viscosity is a volume function only, so that his theory does not fit with these experiments even as well as that of Brillouin, who gives the right sign for $(\partial\eta/\partial\tau)_v$. Just how far η fails of being a pure volume function may be inferred from Figures 7 and 8, plotting log η against volume at 30° and 75° for i-amyl alcohol, ether, and CS_2. I-amyl alcohol, being associated, might be expected to be exceptional, but there is no such reason for the failure of ether and CS_2.

It seems fairly evident from the failure of the previous theories that there is some very important element in the situation not hitherto considered. This I believe to be an interlocking effect between the molecules which prevents the free motion of one layer of molecules over another. Slipping of two interlocking molecules past each other can take place only when haphazard temperature agitation has so far separated them that the interlocking parts are free. According to such a picture, viscosity would be expected to decrease with rising temperature both at constant pressure and constant volume. When the volume is decreased at constant temperature by increasing pressure, a comparatively small decrease of total volume may evidently produce a very large increase of interlocking, and the effect would be expected to increase more and more rapidly as the pressure increases. Furthermore, it is evident that the magnitude of the effect may be very different for different substances.

Such an interlocking effect would be expected to be most important in the most complicated molecules, and strong evidence in favor of such a picture is the very marked tendency found experimentally for the pressure effect to increase as the molecule becomes more complicated. In order to show this I have plotted the increase in log η produced by the first 500 kg. against a number which attempts to give

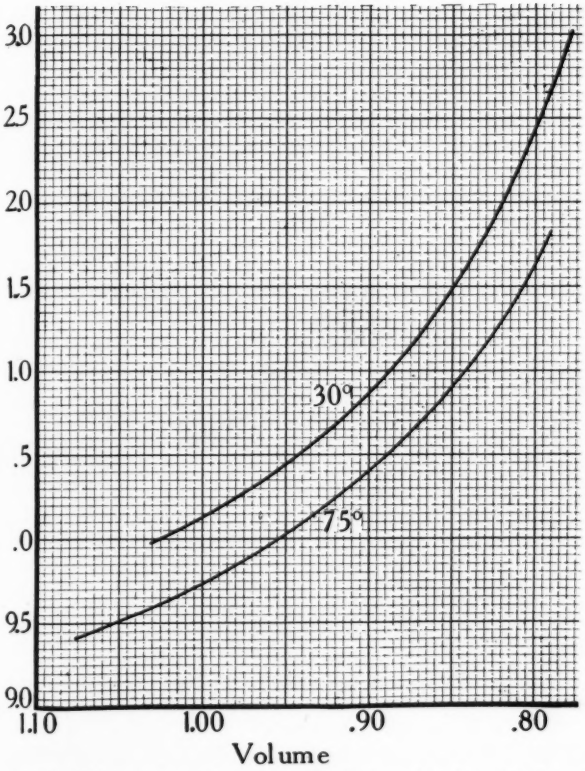

FIGURE 7. The common logarithm of relative viscosity at 30° and 75° of i-amyl alcohol as a function of volume.

some measure of the complication of the molecule. Evidently "complication of the molecule" is a very hazy concept, and any numerical measure of it can be only very crude. It is evident, I think, that the molecule may be more complicated either because it contains more atoms or because the atoms themselves are more complicated. As a measure of the complication of the atom I have taken the number of extra-nuclear electrons (the atomic number), and to measure the complication of the molecule I have multiplied the total

number of extra nuclear electrons in all the atoms which the molecule contains by the total number of atoms in the molecule. We may call such a number the "complexity number." It evidently neglects many factors which we would like to include: for example, no distinction is made between an iso- and a normal alcohol, although our ordinary structural formulas would suggest that the molecule of an iso-alcohol is more likely to interlock with others of its kind than is a molecule of a normal alcohol.

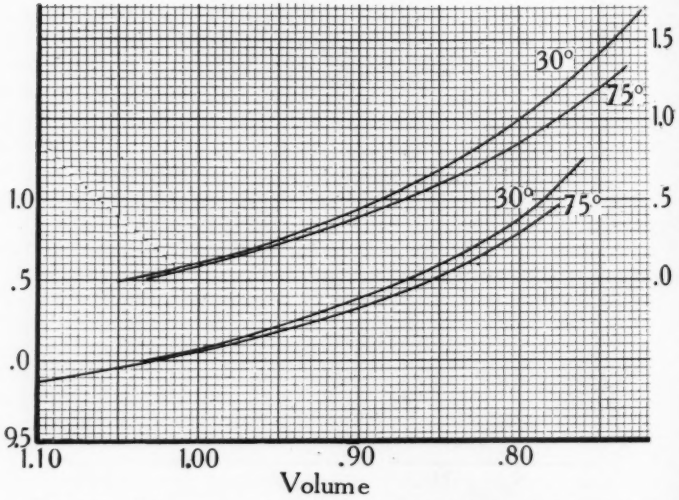

FIGURE 8. The common logarithm of relative viscosity at 30° and 75° of ether and CS_2 as a function of volume. The curves for ether are the upper curves with the scale of ordinates at the right.

In Figure 9 is plotted the effect of 500 kg. on log η against the logarithm of the complexity number. It is evident that there is a correlation which is perhaps as close as could be expected when the extremely arbitrary character of the complexity number is considered and the arbitrariness of comparing the pressure effect for all liquids at the same temperature, 30°, and at low pressures. It must be admitted that the correlation coefficient shown by the figure is not very high, but it will appear more significant if one will take the trouble to

make similar plots against other properties which might be significant. I have not been able to find any other properties of the liquid which show nearly as close a correlation as the complexity number. For instance it has been suspected by some that viscosity in a liquid is due to the attraction between the molecules, which are prevented from moving freely with respect to each other by the attractive forces. If the molecular latent heat of vaporization is taken as a measure of the attractive force, and log η is plotted against it, no correlation whatever will be found. Or one might expect a correlation between absolute viscosity at atmospheric pressure and the pressure effect, but on plotting these two against each other much less correlation will be found than with the complexity number.

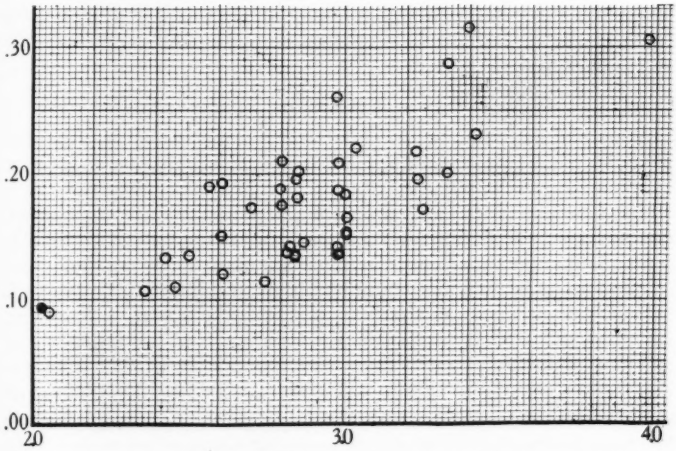

FIGURE 9. The common logarithm of the ratio of the viscosity at 500 kg. to that at atmospheric pressure at 30° C. of all the substances of this paper (except water) plotted as ordinates against the common logarithm of the "complexity number." The complexity number is defined as the product of the number of atoms in the molecule by the number of all the extra-nuclear electrons of the molecule.

If the correlation shown in the figure does not seem sufficiently real, perhaps still stronger evidence of the importance of molecular complexity may be found by confining oneself to a single related series of chemical compounds and noticing the effect of making the molecule

more complicated in the series. Striking examples of this are the increase of pressure effect with molecular weight in the series of alcohols, or of hydrocarbons C_nH_{2n+2}, or the ethyl halogens.

If some such interlocking effect as suggested above is an important part of the viscosity mechanism, this means that so far as viscosity phenomena are concerned the molecule preserves its inviolability and continues to function as a unit when the volume is greatly decreased by high pressure. There are other phenomena, such as compressibility, in which the molecule seems to lose its significance at small volumes, and the atom becomes more significant. A reason for the difference may be seen in the different sorts of relative motion involved. If a molecule ceased to function as a whole during viscous shear it would be torn apart by the relative motion of the parts of the liquid, but the relative motion involved in a hydrostatic compression is not such as to destroy the molecule, even under comparatively large changes of volume.

Summary.

A method has been devised for the measurement of the viscosity of liquids under pressure and applied to 43 pure liquids up to a pressure of 12000 kg./cm.^{2} at 30° and 75° C.

Viscosity increases rapidly with increasing pressure; at low pressures the relation between viscosity and pressure is approximately linear, but at higher pressures viscosity increases much more rapidly. The effect of 12000 kg. may vary from 10 fold to 10^7 fold (excepting water). Log viscosity against pressure is at first concave toward the pressure axis, but above 3000 becomes nearly straight, and for a number of liquids even becomes convex toward the pressure axis. The temperature coefficient of viscosity increases under 12000 kg. by a factor of several fold, varying much with the liquid. Water is exceptional; at low temperature its viscosity decreases with rising pressure, but there is a minimum at about 1000 kg., and from here on the viscosity increases. At higher temperatures its viscosity increases at all pressures, but the increase is very much less than for any of the other liquids measured.

Incidentally a number of new freezing points have been determined under pressure, and the pressure-volume relation for glycerine roughly measured.

No theory proposed hitherto is adequate to account for these pressure phenomena. It is suggested that an interlocking effect between the molecules is an important element in the situation, an idea which

is supported by the rapid increase of the pressure effect as the molecule becomes more complicated.

It is a pleasure to acknowledge the assistance given by my mechanic Mr. E. T. Richardson in setting up the apparatus and making many of the readings.

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BOILING POINTS OF LIQUIDS FROM EASTMAN KODAK CO.,
SEE PAGE 73

n-propyl alcohol	96–98 C.
i-butyl alcohol	106–108
i-amyl alcohol	130–132
n-hexane	68–69
n-octane	124–126
i-amyl-decane	156–158
Ethyl chloride	12.5–13
Ethyl bromide	38–40
Ethyl iodide	71–72
Acetone	55.5–55.8
Cineole	53–54 at 8 mm.
Oleic Acid	U.S.P.
Aniline	mpt. —6
Diethyl aniline	102–104 at 10 mm.
Nitro benzene	mpt. 5
O-xylene	143.5–144.5
m-xylene	138–139
p-cymene	176.5–177.5
Eugenol	135–140 at 15 mm.